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$Mn_2(CO)_6(\mu\text{-}CO)(\mu\text{-}S_2)$: The Simplest Disulfide of Manganese Carbonyl

Richard D. Adams,*,† O-Sung Kwon, and Mark D. Smith

Department of Chemistry and Biochemistry, University of South Carolina, Columbia, South Carolina 29208

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$Fe_2(CO)_6(\mu\text{-}S_2)$, the simplest disulfide of iron carbonyl, was first reported by Hieber over 40 years ago.[1] It has a rich reaction chemistry and has been extensively investigated over the years.[2] Curiously, the related manganese compound $Mn_2(CO)_6(\mu\text{-}CO)(\mu\text{-}S_2)$, **1**, has not yet been reported. Because of the importance of bridging sulfido ligands in the synthesis of polynuclear metal complexes in inorganic[3] and bioinorganic systems,[4] we have set out to prepare **1** and to study its structure and reactivity.

The new compound **1** was obtained in 36% yield from the reaction of $Mn_2(CO)_9(NCMe)$ with thiirane in hexane solvent at 25 °C for 24 h.[5] The product was isolated by chromatography on silica gel by using a hexane/CH_2Cl_2 (3/1, v/v) solvent mixture for elution. The infrared spectrum of **1** shows a low-energy absorption at 1894 cm^{-1} that can be attributed to a bridging carbonyl ligand. The ^{13}C NMR spectrum at −25 °C shows three resonances in a 212.5 (2 CO), 213.5 (4 CO), and 236.5 (1 CO) pattern with the last also attributable to a bridging carbonyl ligand. Details of the molecular structure of **1** were established by a single-crystal X-ray diffraction analysis.[6] An ORTEP diagram of the molecular structure of **1** is shown in Figure 1. Like $Fe_2(CO)_6(\mu\text{-}S_2)$, **1** contains two $M(CO)_3$ units joined by a metal−metal single bond, 2.6745(5) Å. The Mn−Mn distance is considerably shorter than that observed in $Mn_2(CO)_{10}$, 2.9038(6) Å.[7] This can be attributed to the presence of the two supplemental bridging ligands, one S_2 ligand and one CO ligand. An even shorter Mn−Mn distance, 2.581(1) Å, was found in the compound $Mn_2(CO)_4(PMe_3)_2(\mu\text{-}CO)(\mu\text{-}SMe)_2$,[8] which contains two bridging methylthiolato ligands and a bridging CO ligand. The bridging S_2 ligand in **1** is similar to that found in $Fe_2(CO)_6(\mu\text{-}S_2)$. Both sulfur atoms are bonded to both metal atoms, and the S−S bond is perpendicular to the Mn−Mn bond. The S−S bond length in **1** at 2.0474(11) Å is slightly longer than that found in $Fe_2(CO)_6(\mu\text{-}S_2)$, 2.021(3) Å[9a] and 2.007(5) Å.[9b]

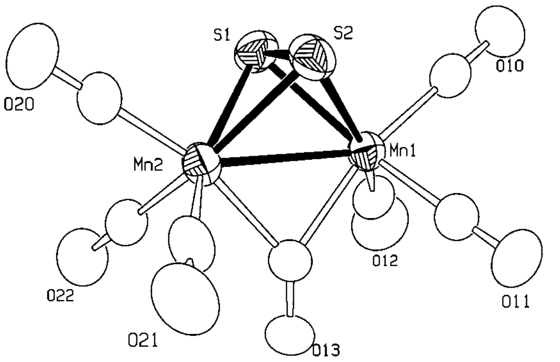
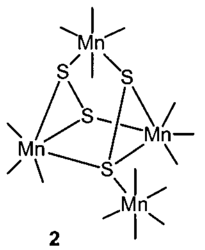


Figure 1. An ORTEP diagram of the molecular structure of $Mn_2(CO)_7(\mu\text{-}S_2)$, **1**, showing 40% probability thermal ellipsoids. Selected interatomic distances (Å): Mn(1)−Mn(2) = 2.6745(5), Mn(1)−S(1) = 2.2890(8), Mn(1)−S(2) = 2.2877(7), Mn(2)−S(1) = 2.2855(8), Mn(2)−S(2) = 2.2842(8), S(1)−S(2) = 2.0474(11), Mn(1)−C(13) = 2.033(3), Mn(2)−C(13) = 2.084(3).

Two minor products identified as of $Mn_4S_4(CO)_{15}$, **2** (4% yield), and $Mn_4S_4(CO)_{14}(NCMe)$, **3** (6% yield), by a combination of IR, NMR, and single-crystal X-ray diffraction analyses[11] were also obtained from the reaction that gave **1**.[5] Compound **2** was obtained previously by oxidative removal of the $SnMe_3$ groups from $Mn_2(CO)_8(\mu\text{-}SSnMe_3)_2$ by using iodine.[10] It was proposed that **2** was formed in that reaction by the dimerization of two incipient molecular units of "$Mn_2(CO)_8(\mu\text{-}S_2)$" formed by cleavage of the



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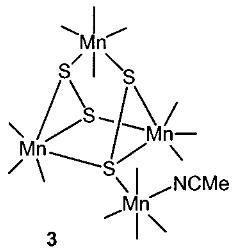

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† E-mail: Adams@mail.chem.sc.edu.

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(5) A 98.0 mg amount (0.243 mmol) of $Mn_2(CO)_9(NCMe)$ was allowed to react with 30.0 μL (2 equiv) of thiirane in 100 mL of hexane at 25 °C for 24 h. The products were separated by column chromatography on silica gel using a hexane/CH_2Cl_2 (3/1) solvent mixture to yield 32.6 mg (36%) of $Mn_2(CO)_6(\mu\text{-}CO)(\mu\text{-}S_2)$, **1**, 3.9 mg (4%) of $Mn_4S_4(CO)_{15}$, **2**, and 5.6 mg (6%) of $Mn_4S_4(CO)_{14}(NCMe)$, **3**, in this order of elution. Spectral data for **1**: IR ν_{CO} (cm^{-1} in hexane): 2079 (w), 2044 (vs), 2007 (m), 1982 (vs), 1946 (vw), 1894 (w). ^{13}C NMR (−25 °C, d_8-toluene): 212.5, 213.5, and 236.5. Anal. Calcd: C, 22.71. Found: C, 23.29. Spectral data for **2**: IR ν_{CO} (cm^{-1} in hexane): 2140 (w), 2091 (m), 2065 (vs), 2031 (m), 2024 (vs), 2014 (s), 2008 (s), 1983 (m), 1958 (m), 1949 (w), 1934 (m), 1919 (w). Anal. Calcd: C, 23.45. Found: C, 23.54. Spectral data for **3**: IR ν_{CO} (cm^{-1} in hexane): 2116 (w), 2091 (m), 2047 (vs), 2036 (vs), 2021 (vs), 2010 (vs), 1997 (vs), 1979 (s), 1948 (s), 1939 (m), 1922 (m), 1907 (w). ^1H NMR ($CDCl_3$): 2.58 (bs, 3H). Anal. Calcd: C, 24.60; H, 0.38. Found: C, 24.46; H, 0.35.

(6) X-ray intensity data were measured at 293 K on a Bruker SMART APEX CCD-based diffractometer using Mo Kα radiation (λ = 0.71073 Å). Crystal data for **1**: crystal system, orthorhombic; space group, $P2_12_12_1$; a = 6.8528(6) Å, b = 10.0584(9) Å, c = 17.3064(15) Å, Z = 4, μ = 2.485 mm^{-1}, reflections 2442 ($I > 2\sigma(I)$), GOF = 1.257, R1 = 0.0257, wR2 = 0.0601.

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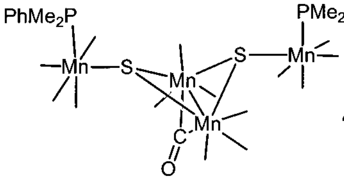
$SnMe_3$ group from the sulfur atoms. Our studies support the idea of the involvement of "$Mn_2(CO)_8(\mu\text{-}S_2)$" species. For example, when **1** was treated with CO, it was converted to **2** in 90% yield in 24 h at 25 °C. The addition of one CO to one molecule of **1** should yield a "$Mn_2(CO)_8(\mu\text{-}S_2)$" species. A subsequent coupling of this "$Mn_2(CO)_8(\mu\text{-}S_2)$" to a second equivalent of **1** could then yield **2** after some minor rearrangements. Compound **3** is simply an NCMe derivative of **2**.

Interestingly, the reaction of **1** with phosphines does *not* lead to CO ligand substitution products, but instead leads to a higher nuclearity species containing bridging sulfido ligands. For example, the reaction of **1** with 1 equiv of PMe_2Ph at 25 °C gave the new compound $Mn_4S_2(CO)_{15}(PMe_2Ph)_2$, **4**, in 37% yield.[12] The molecular structure of compound **4** was established crystallographically and is shown in Figure 2.[13] Overall, the molecule contains a crystallographically imposed C_2 rotation axis. Like **1**, compound **4** contains an $Mn_2(\mu\text{-}S)_2$ core with an Mn−Mn single bond, but this bond at 2.6356(16) Å is slightly shorter than that in **1**. In **4**, however, the sulfur atoms are not mutually bonded, S···S = 2.829(2) Å. Instead, each sulfur atom contains an $Mn(CO)_4(PMe_2Ph)$ substituent. There is also a bridging carbonyl ligand, $\nu_{CO} = 1933\ cm^{-1}$. While the mechanism of the formation of **4** is not yet known, the presence of four manganese atoms clearly implies the involvement of 2 equiv of **1** with the loss of two sulfur atoms. The fate of the sulfur atoms was established spectroscopically to be in the form of S═PMe_2Ph by a combination with PMe_2Ph.



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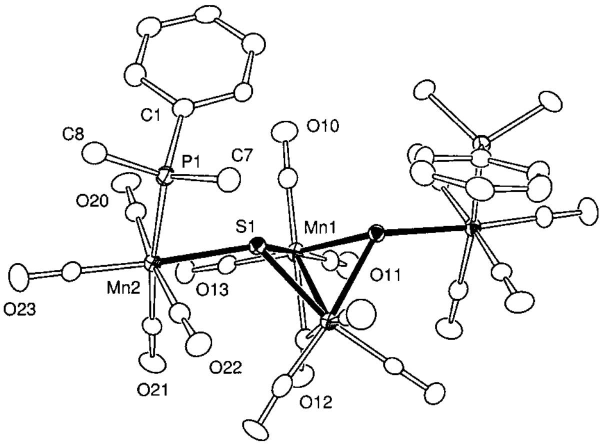

Figure 2. A side view of the molecular structure of $Mn_2(CO)_{14}(PMe_2Ph)_2(\mu\text{-}S)_2$, **4**, showing 40% probability thermal ellipsoids. Selected interatomic distances (Å): Mn(1)−Mn(1′) = 2.6356(16), Mn(1)−S(1) = 2.3458(15), Mn(1)−S(1′) = 2.3449(15), Mn(2)−S(1) = 2.3992(14), Mn(2)−P(1) = 2.3480(16), S(1)···S(1′) = 2.829(2), Mn(1)−C(12) = 2.058(6).

The stable new compound **1** should be a valuable reagent for the synthesis of other sulfur-containing manganese carbonyl complexes. In addition, it will be interesting to see how the organic chemistry of the disulfido ligand in **1** compares and contrasts with that observed for $Fe_2(CO)_6(\mu\text{-}S_2)$.[2,14]

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Supporting Information Available: Crystallographic data in CIF format for **1**−**4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(11) Crystal data for **2**: crystal system, orthorhombic; space group, $P2_1/c$; a = 9.3161(7) Å, b = 15.5165(11) Å, c = 18.1976(13) Å, β = 96.028(2)°, Z = 4, μ = 2.273 mm^{-1}, reflections 5363 ($I > 2\sigma(I)$), GOF = 0.908, R1 = 0.0374, wR2 = 0.0745. Crystal data for **3**: crystal system, monoclinic; space group, $P2_1/c$; a = 9.6193(16) Å, b =16.0585(19) Å, c =18.3494(31) Å, β = 101.002(14)°, Å, Z = 4, μ = 2.14 mm^{-1}, reflections 2582 ($I > 3\sigma(I)$), GOF = 1.045, R1 = 0.0324, wR2 = 0.0538.

(12) An 84.5 mg (0.2285 mmol) amount of **1** was allowed to react with 32.5 μL (0.2285 mmol) of PMe_2Ph in 30 mL of hexane at 25 °C for 2 h. $Mn_4S_2(CO)_{15}(PMe_2Ph)_2$, **4** (45.3 mg, 37% yield), precipitated and was isolated by filtration. The product was recrystallized from a hexane/CH_2Cl_2 solution by cooling. IR ν_{CO} (cm^{-1} in CH_2Cl_2): 2081 (m), 2069 (s), 2016 (vs), 1960 (m), 1933 (s). ^{1}H NMR (CD_2Cl_2): δ 7.48−7.69 (m, 10H), 2.07 (d, $^3J_{P-H}$ = 9 Hz, 12H). ^{31}P NMR ($CDCl_3$): δ 15.0 (s). Anal. Calcd: C, 36.08; H, 2.27. Found: C, 36.69; H, 2.12.

(13) Crystal data for **4**: crystal system, orthorhombic; space group, $Fdd2$; a = 27.827(2) Å, b = 33.959(3) Å, c = 9.4488(7) Å, Z = 4, μ = 1.573 mm^{-1}, 4559 reflections ($I > 2\sigma(I)$), GOF = 1.045, R1 = 0.0504, wR2 = 0.1331.

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